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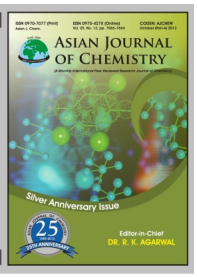

Influence of COD/SO_4^{2-} Ratios on Performance of Anaerobic Hybrid Reactor and Up-Flow Anaerobic Sludge Bed Reactor

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This study was carried out to be able to provide possible key parameters for the best performance of anaerobic hybrid reactor and up-flow anaerobic sludge bed reactor (UASBR). Laboratory-scale (1.70 L) anaerobic hybrid reactor and UASBR were operated at chemical oxygen demand (COD) to sulfate (SO_4^{2-}) ratios of 25, 15, 10, 7 and 5 in a 155-day period to evaluate the effects of the presence of sulfate on the reactor performance. The results showed that when COD/SO_4^{2-} ratios changed from 25 to 5 with increasing sulfate concentration from 400 to 2130 mg/L, slight decreases both in conversion ratios of removed chemical oxygen demand to methane and chemical oxygen demand removal efficiencies were observed. However, with decreased COD/SO_4^{2-}, methane production rate decreased considerably and sulfate removal efficiencies increased. For UASBR, the methane production rate decreased as much as about 59 % and high sulfate removal efficiencies were obtained at COD/SO_4^{2-} ratio of 5. Chemical oxygen demand removal efficiencies and biogas produced from the anaerobic hybrid reactor were always higher compared to those obtained with UASBR.

Key Words: Anaerobic hybrid reactor, Up-flow anaerobic sludge bed, Sulfate removal, Methane, COD/SO_4^{2-} ratio.

INTRODUCTION

Sulfate has been present in a variety of industrial effluents such as acid mine drainage, molasses wastewater, domestic sewage, textile wastewater, molasses fermentation and potato starch[1-3]. Sulfate can be removed from wastewaters at significant costs by chemical precipitation or desalination processes such as reverse osmosis and ion exchange. On the other hand, the success of high-rate anaerobic technology has encouraged researchers to extend its application to the treatment of complex wastewaters. Consequently, increasing attention has been given to anaerobic processes for the removal of sulfate from industrial wastewaters. A variety of reactors have been reported for wastewater treatment promoted by sulfate-reducing bacteria, such as anaerobic filters, batch reactors, baffled reactors, fixed bed reactors, "gas-lift" reactors, fluidized bed reactors and expanded granular sludge bed reactors[4]. The anaerobic hybrid reactor and up-flow anaerobic sludge blanked reactor (UASBR) have been considered as potential alternatives for wastewater treatment[5]. Up-flow anaerobic sludge bed reactor reactors and anaerobic hybrid reactor are examples of successful units, which were used for the treatment of sulfate-rich wastewater[6].

High concentration of sulfate in wastewater has a detrimental effect on the anaerobic treatment due to preferential reduction of sulfate and subsequent terminal product formation by the fermentation reaction. Sulfate-reducing bacteria, as the name implies, are special anaerobes that include a heterogeneous assemblage of microorganisms and their role is analogous to that of methane producing bacteria (MPB) that form CH_4 and CO_2 as anaerobic end products[7-11]. The growth of sulfate-reducing bacteria (SRB) is dependent on the carbon and sulfate concentration, whereas the growth of methane producing bacteria is solely dependent on the concentration of carbon, *i.e.*, acetate[12].

It is important to investigate the factors that affect the competition between sulfate-reducing bacteria and methane producing bacteria communities in order to improve the anaerobic treatment of these wastewaters[13]. The outcome of this competition can determine the composition of the biogas produced or conversion ratios of removed chemical oxygen demand to methane in bioreactors[2].

The COD/SO_4^{2-} ratio in wastewater is an important controlling parameter for electron flow in anaerobic fermentation. Mizuno *et al*[14]. reported that when COD/SO_4^{2-} ratio was higher than 6, methanogens predominated, but at COD/SO_4^{2-} ratios less than 1.5, sulfate-reducing bacteria were more competitive, resulting in a significant increase of free H_2S that severely affects methanogens but not sulfate reducers. Studies focusing on COD removal in effluents with low COD/SO_4^{2-} ratio are scarce in literature.

The aim of this work was studying the effect of six different COD/SO_4^{2-} ratios (25, 15, 10, 7 and 5) on the performance of laboratory-scale anaerobic hybrid reactor and UASBR, seeded with non-sulfate-adapted methanogenic sludge treating synthetic wastewater.

EXPERIMENTAL

The anaerobic hybrid reactor and UASBR systems used in this study were produced from pipe (inner diameter 5.5 cm, height 66 cm and thickness 1.2 cm) made of PVC. The active working volumes of the reactors were 1700 mL. Gas accumulation funnels were placed at the top of the reactors.

Fig. 1 schematics of anaerobic hybrid reactor and UASBR (1), influent; (2), peristaltic pump; (3), anaerobic hybrid reactor; (4), UASBR; (5), sludge bed; (6), anaerobic hybrid reactor media with height 22 cm; (7), effluent; (8), siphon arrangement for effluent; (9) gas storage balloon; (10) liquid displacement system (11), gas pump.

A schematic of the anaerobic hybrid reactor and UASBR systems is illustrated in Fig. 1. Feeding was provided with a multichannel peristaltic pump (Watson Marlow, Model 205S/CA12). Basalt, a natural material, was used as the filling material; with diameters of 2.38-4.36 mm. Total filling height over total filling weight was chosen 1/3. The reactors were placed in a heating room. The reactors were run with mesophylic conditions (37 ± 1 °C).

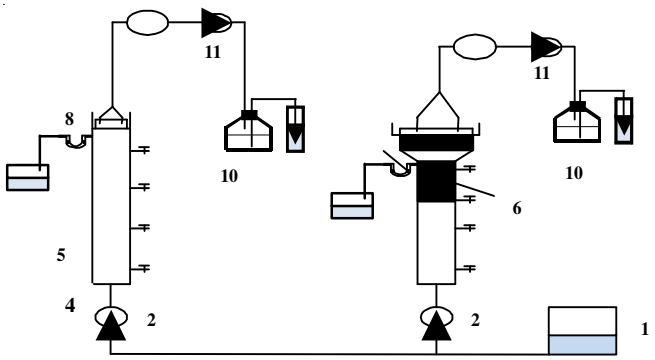

Fig. 1. Schematics of anaerobic hybrid reactor and UASBR. (1), influent; (2), peristaltic pump; (3), anaerobic hybrid reactor ; (4), UASBR; (5), sludge bed; (6), anaerobic hybrid reactor media with height 22 cm.; (7), effluent; (8), siphon arrangement for effluent; (9), gas storage balloon; (10), liquid displacement system (11), gas pump

Substrate and seed sludge: Formulation of synthetic wastewater, which is used as a carbon source, is provided in Table-1. This solution is equivalent to 5000 ± 40 mg COD/L[15].

TABLE-1
COMPONENTS OF SYNTHETIC WASTEWATER
(5000 ± 40 mg COD/L)[15]

Components	mg/L
Bacteriological peptone	1000
Glucose	3400
Meat extract	700
Sodium bicarbonate ($NaHCO_3$)	3000
Calcium chloride ($CaCl_2.2H_2O$)	48.2
Magnesium sulfate ($MgSO_4.7H_2O$)	53.2
Ammonium chloride (NH_4Cl)	400
Ferro sulfate ($FeSO_4.7H_2O$)	40
Potassium dehydrogen orthophosphate (KH_2PO_4)	200

In this study, the COD concentration in synthetic wastewater was 10000 ± 240 mg/L and sulfate concentration was increased from 400, 690, 1040, 1490 and 2130 mg/L by using magnesium sulfate ($MgSO_4 \cdot 7H_2O$). COD/N/P ratio of the synthetic wastewater fed to the reactors varied between 146/6.8/1 and 155/6/1. The synthetic substrate was prepared daily and the contents of the feed tank were continuously stirred with mechanical agitator and fed into the rectors by the peristaltic pump.

Analysis: Each of the reactors for COD, alkalinity and mixed liquid volatile suspended solids (MLVSS), was analyzed according to standard methods[16]. During our study, sulfate amount (Equipment number: 14791) was determined using Nova 60 Spectraquant® (Merck) test equipments. The pH was measured with pH-meter made by ORION (Model 420A). Temperature and pH were monitored daily. Adjustment of pH was made by using 0.1 N NaOH solutions when the pH fell below 6.

A liquid displacement method was employed for total gas measurements. The percentage of methane in biogas was analyzed using gas chromatographic system (Model GC-14 B) equipped with a thermal conductivity detector and a 1.5 m stainless column packed with 45/60 Carboxen-1000. The operational temperatures of the injection port and the detector were kept at 130 °C and 150 °C, respectively. Helium was used as the carrier gas at a flow rate of 30 mL/min. Analytic methane standard (Fluka, Catalog No: 02329) was used in the analyses carried out with gas chromatography.

RESULTS AND DISCUSSION

Acclimatization and start-up: The seed sludge was obtained from the UASBR of a beer factory wastewater in Adana, Turkey. The anaerobic hybrid reactor and UASBR were inoculated with 15 g/L MLSS of volume. The reactors were filled with active seeds (33 % v/v) and the remaining with the synthetic wastewater and run in batch mode for a 7 day period for acclimatization. The reactors were started using 3000 mg COD/L synthetic wastewater as substrate and afterwards the dilution was gradually decreased to acclimatize the biomass for higher concentrations of synthetic wastewater.

The start-up period for both anaerobic hybrid reactor and UASBR was 30 days. Steady state was defined based on the consistent COD removal efficiency. Reactors were fed with synthetic wastewater of 5000 ± 40 mg/L COD concentration during the start-up period. During the whole period of study, anaerobic hybrid reactor and UASBR were operated continuously with a constant HRT of 24 h. COD removal efficiencies and conversion ratios during the start-up period for both of the reactors are shown in Fig. 2.

Effect of COD/SO_4^{2-} ratio on the performance of anaerobic hybrid reactor and UASBR: After stable states were obtained in the system, we did not observe any decrease in the pH levels. System parameters were measured to follow the efficiency of the reactors and remove the organic compounds at steady state. Biogas production rate was measured during different operating conditions and the conversion rates of removed COD to methane were calculated. Methane contents of the biogas produced in the anaerobic hybrid reactor and UASBR were 78.7 ± 3.8 and 71.2 ± 3.2%, respectively. The amount of biogas produced from the anaerobic hybrid reactor was always higher compared to the UASBR.

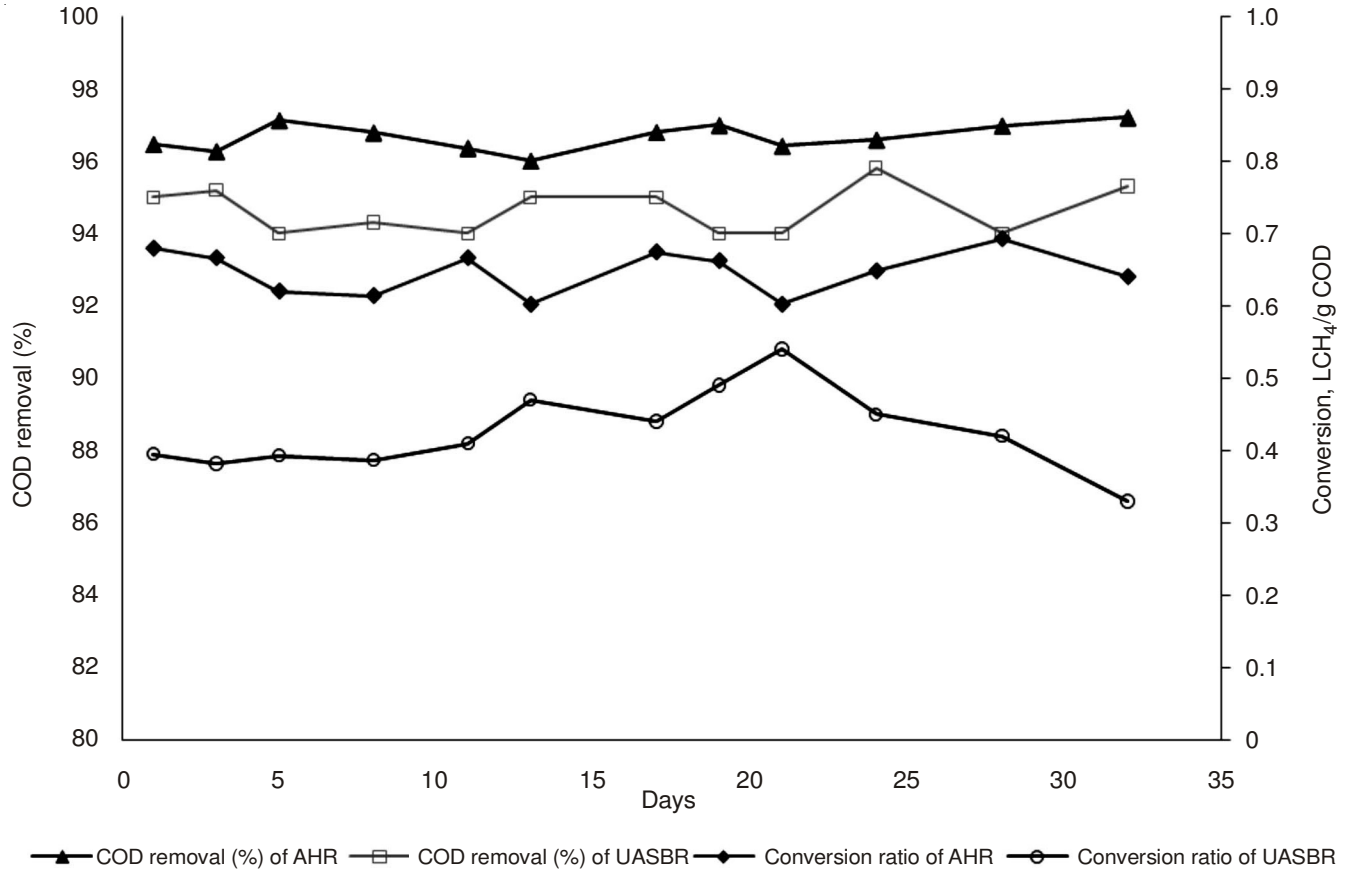

Fig. 2. COD removal efficiencies and conversion ratios of the start-up period for anaerobic hybrid reactor and UASBR

In the operational state, reactors were operated as HRT at 24 h, COD concentration at 10000 mg/L and OLR at 10 kg COD/m^3 day. During the experimental studies, alkalinity was measured as a lot higher than the minimum level of 1000 mg $CaCO_3$/L, which is required for the development of methane bacteria[17]. The effects of different COD/SO_4^{2-} ratios ranging from 25 to 5 were studied in anaerobic hybrid reactor and UASBR by varying the sulfate concentration of the influent. Each COD/SO_4^{2-} ratio was evaluated for about 25 days. The efficiencies of the reactors for different COD/SO_4^{2-} ratios are presented in Fig. 3. The results in Fig. 3 clearly show that the anaerobic hybrid reactor provided a better removal for COD as compared to the UASBR and moreover the performance of the anaerobic hybrid reactor was more stable.

During the first phase (COD/SO_4^{2-} = 25) in anaerobic hybrid reactor, the conversion rates of removed COD to methane varied strongly between 0.312 and 0.464 L CH_4/g COD_r. During the time frame between 35th and 59th days when COD/SO_4^{2-} was 25, the COD removal efficiencies were about 95 % in anaerobic hybrid reactor and UASBR. After decreasing COD/SO_4^{2-} ratio to 15, the COD removal efficiency decreased to about 92 % for the UASBR. In contrast to UASBR, COD removal efficiency in anaerobic hybrid reactor was not affected. Conversion ratios of removed COD to methane at both of the rectors were about 0.30 (Fig. 4).

The COD/SO_4^{2-} ratio in effluents appears to be a key factor in the regulation of the competition between methanogenic and sulfate-reducing bacteria[18-20]. Process failures of anaerobic reactors for methane generation have been reported when the COD/SO_4^{2-} ratio[21] of the wastewater was less than 10. From data presented in Fig. 3, it can be deduced that the decrease of COD/SO_4^{2-} ratio from 15 to 10 had a little negative effect on COD removal efficiency. The gradual decline in COD removal efficiency could be a result of the effects of foaming in the reactor sludge. In our study, when the COD/SO_4^{2-} ratio was about 10 (between days 85-110), over 90 % COD removal efficiency was obtained at anaerobic hybrid reactor. In this period, COD removal efficiency of UASBR varied between 85-90 %. In these conditions, methane production decreased 0.22 L CH_4/g COD_r in the UASBR whereas in the anaerobic hybrid reactor, the decrease in production was almost 0.28 L CH_4/g COD_r.

After this point (between days 110-133, Fig. 3), there was a sharp decline in COD removal efficiency at UASBR in contrast to anaerobic hybrid reactor when COD/SO_4^{2-} decreased to 7. In this situation (COD/SO_4^{2-} = 7), low COD removal efficiencies (under 80 %) were obtained at UASBR. The removal efficiency of COD of the anaerobic hybrid reactor was more stable (about 90 %). At the end of experimental studies, COD/SO_4^{2-} ratio was decreased to 5. In this condition, while the anaerobic hybrid reactor removed about 85 % of the COD, the UASBR removed about 65 % of COD. In these conditions, methane production at anaerobic hybrid reactor and UASBR decreased to 0.14 and 0.06 L CH_4/g COD_r, respectively.

As a consequence of the decrease in COD/SO_4^{2-} ratio from 7 to 5, there was stronger adaptation of the biomass in the reactors, highlighted by a high degradation yield of organic compounds in the presence of sulfate. In both reactors methane

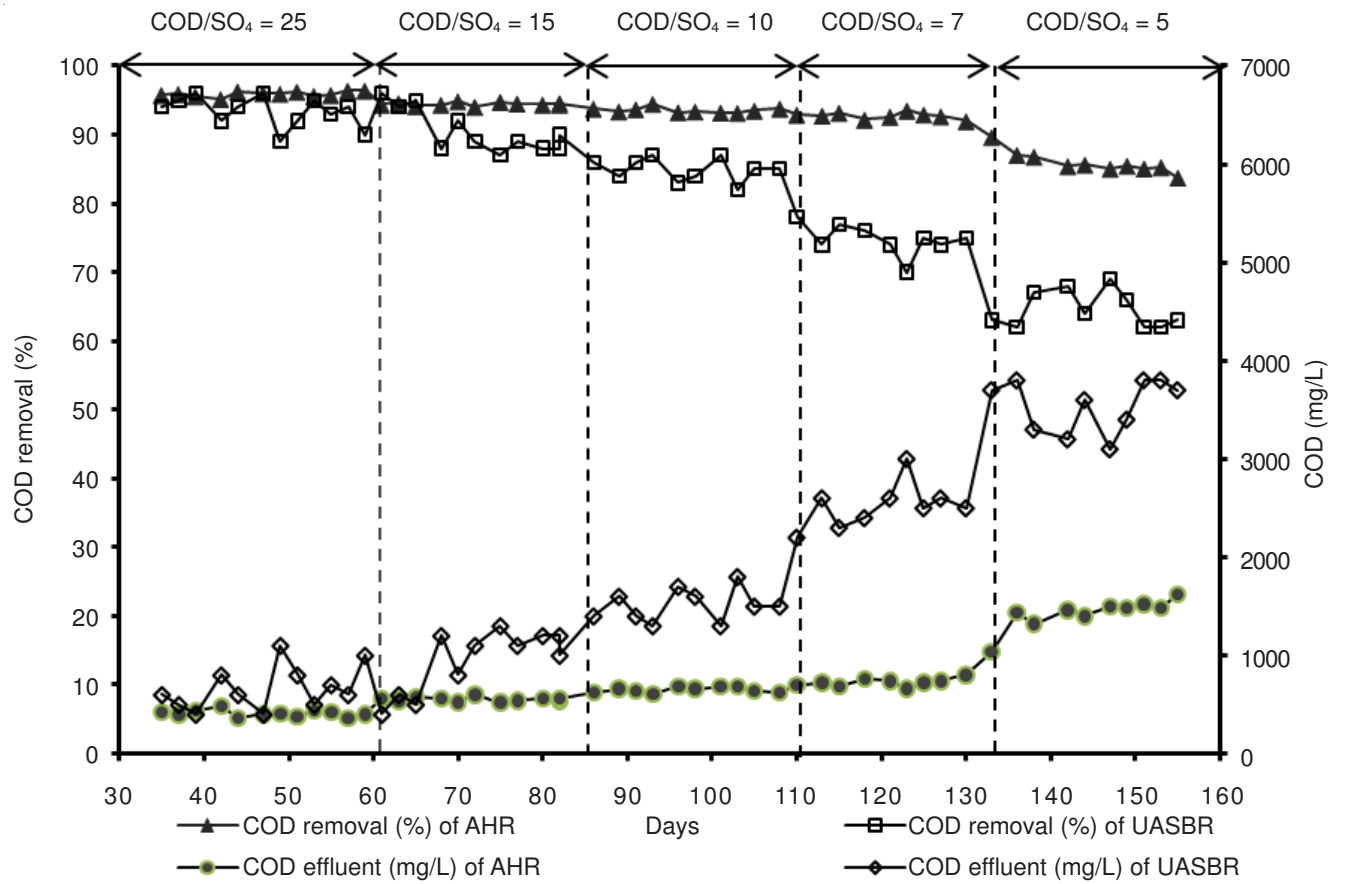

Fig. 3. COD removal efficiency and effluent COD concentrations for anaerobic hybrid reactor and UASBR at the different COD/SO_4^{2-}

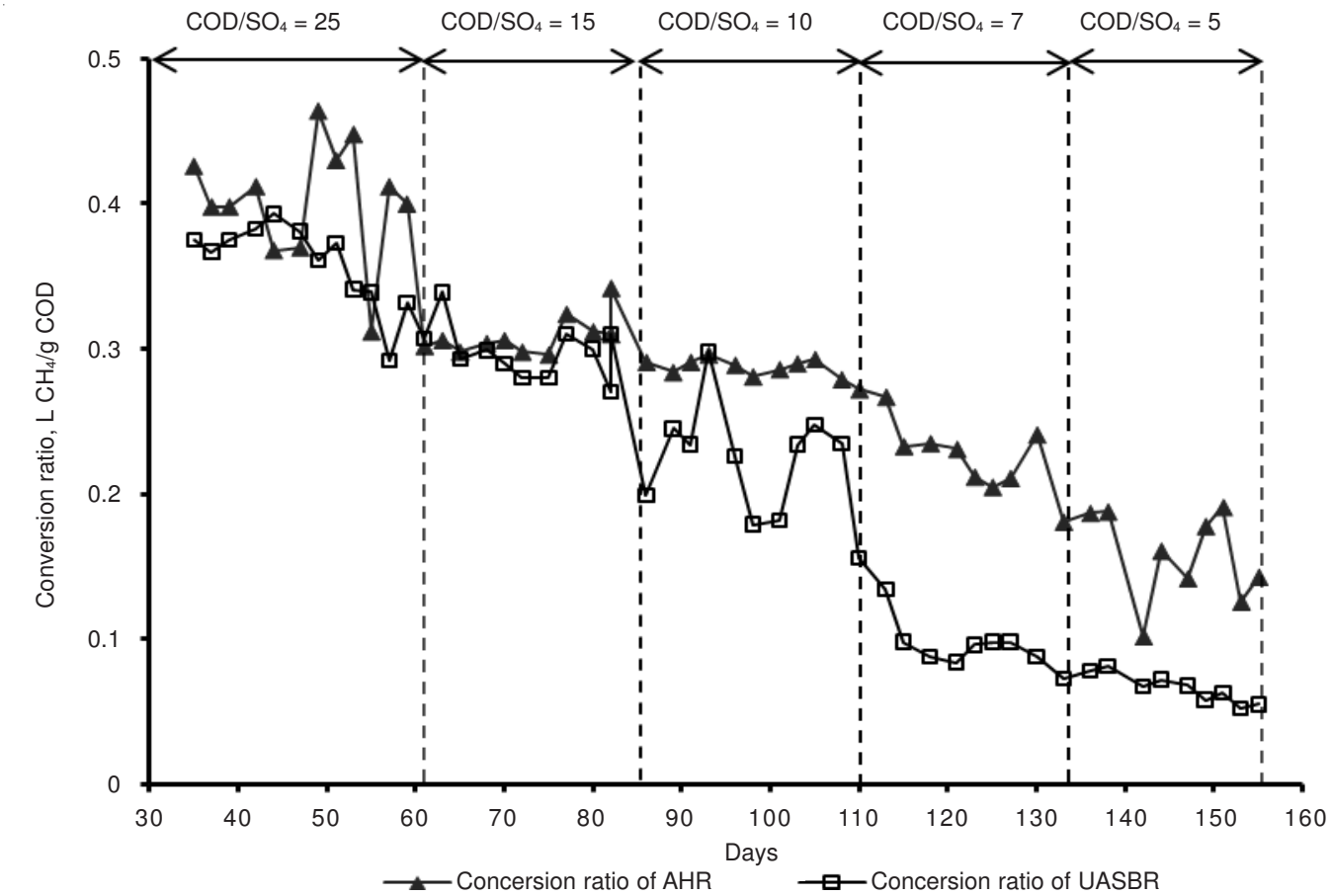

Fig. 4. Conversion ratios of removed COD to methane at anaerobic hybrid reactor and UASBR

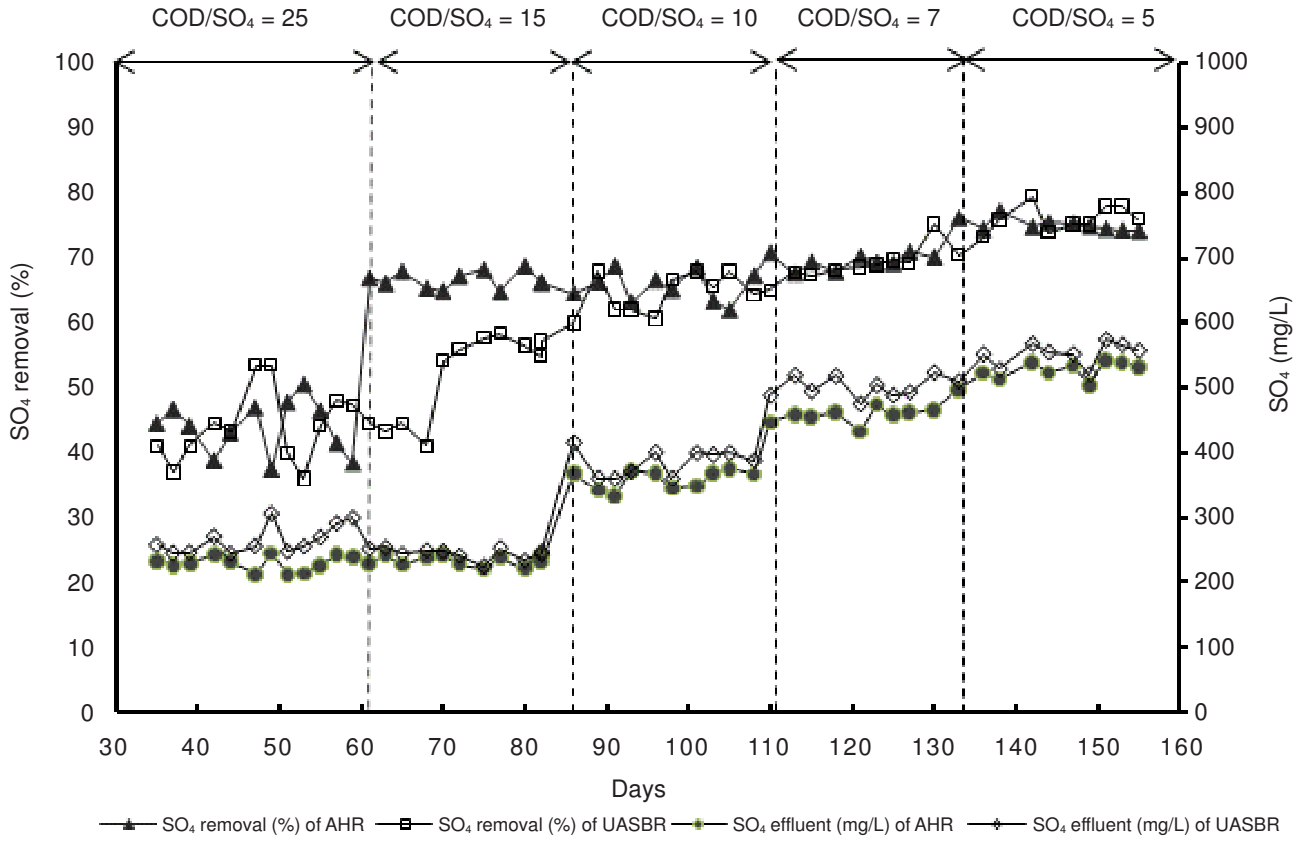

Fig. 5. Effluent sulfate concentrations and sulfate removal efficiencies at anaerobic hybrid reactor and UASBR

production was the most critically affected parameter due to the toxicity of SO_4^{2-}. Nevertheless, the methanogenic performance of anaerobic hybrid reactor and UASBR was fairly different (Fig. 4), where a great difference in methanogenesis inhibition in relation to the COD/SO_4^{2-} rate can be observed. Fig. 5 shows effluent sulfate concentrations and sulfate removal efficiencies at anaerobic hybrid reactor and UASBR; when the COD/SO_4^{2-} ratio decreased from 25 to 5, sulfate removal efficiency increased with the decrease in COD/SO_4^{2-} ratio and the increase influent sulfate concentration.

Removing[22] 1 g of SO_4-S requires 2 g of COD and the conversion rates for each of the COD/SO_4^{2-} rates showed a correlation y = 0.1469 ln(x) - 0.0572, (R^2) of 0.929 at anaerobic hybrid reactor and y = 0.1272 ln(x) - 0.0685, (R^2) of 0.9336 at UASBR with a slope close to 1 (Fig. 6).

Previous research has shown that lowering the COD/SO_4^{2-} ratio from 6 to 0.34 rapidly favored sulfate reduction *vs.* methanogenesis in a methanol-fed thermophilic bioreactor[23]. A similar study monitored anaerobic sulfate reduction in a fixed bed reactor with pal-rings as filling material and using glucose as organic substrate. Effluent COD and sulfate concentrations were 7.63 g/L and 2.9 g/L, respectively, giving a COD/SO_4^{2-} ratio of 2.6. The reactor achieved only 47 % COD removal and 39 % sulfate reduction efficiencies[24]. Similar results were obtained in this study with basalt as a filling material, with 91 % COD removal and 87 % sulfate reduction efficiencies. Initial effluent COD and sulfate concentration were 8.25 g/L and 7 g/L, respectively.

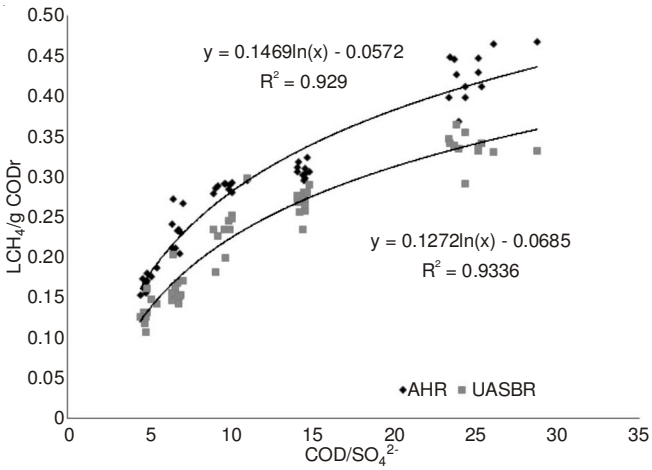

Fig. 6. Relationship between COD/SO_4^{2-} and conversion rate of the anaerobic hybrid reactor and UASBR

Shayegan *et al.*[25] reported similar results in an up-flow anaerobic sludge bucket (UASB) reactor after increasing COD/SO_4^{2-} ratio to 2, resulting in 85 % COD removal efficiency and 82 % sulfate reduction, probably due to the comparable experimental data (both anaerobic reactors were thermophilic and neutrophilic, using sodium sulfate as sulfate source and comparable COD/SO_4^{2-} ratios.

Choi *et al.*[26] reported that at COD/SO_4^{2-} ratios exceeding 2.7, a negative effect on the sulfate-reducing bacteria activity can be observed because methanogenic archaea (MA) can compete with sulfate-reducing bacteria for hydrogen and

acetate. In a similar study, El bayoumy *et al*.[27] suggested that COD/SO_4^{2-} ratios between 1.5 and 2.25 were enough to attain the highest hydrogen sulfide production when lactate or acetate was used as carbon and electron sources.

Conclusions

Comparison of anaerobic hybrid reactor with UASBR shows that anaerobic hybrid reactor may be a good option for sulfate reduction of wastewaters treated with additional advantages of good quality COD removal efficiencies and biogas production. Performances of anaerobic hybrid reactor and UASBR at constant concentration of COD (COD = 10000 mg/L) but with different ratios of COD/SO_4^{2-} were investigated and the following results were obtained:

(1) High removal efficiencies could be obtained with COD/SO_4^{2-} ratio of 25. When COD/SO_4^{2-} ratios were decrease from 25 to 5, with increasing sulfate concentration, COD conversion ratios and COD removal efficiencies decreased but a slight increase in sulfate removal efficiencies were observed.

(2) When sulfate concentration was below 1040 mg/L, inhibition was not observed.

(3) With increase of sulfate concentration up to 2130 mg/L, slight decrease of COD removal was observed.

(4) Basalt can be considered an effective packing material for biomass attachment, especially for methanogenic archeae and sulfate reducing bacteria.

(5) When anaerobic hybrid reactor is compared to UASBR for different COD/SO_4^{2-} ratios, sulfate reduction was almost the same. Though COD removal efficiency was higher for anaerobic hybrid reactor. Lower COD/SO_4^{2-} ratios affected higher methane production for anaerobic hybrid reactor.

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REFERENCES

1. E. Colleran, S. Finnegan and P. Lens, *J. Genet. Mol. Microbiol*., **67**, 29 (1995).
2. P.N.L. Lens, A. Visser, A.J.H. Janssen, L.W.H. Pol and G. Lettinga, *Crit. Rev. Environ. Sci. Technol*., **28**, 41 (1998).
3. J.W.H. Stefanie, O. Elferink, A. Visser and L.W. Hulshoff Pol, *FEMS Microbiol. Rev*., **15**, 119 (1994).
4. A. Sarti, A.J. Silva, M. Zaiat and E. Foresti, *Desalination*, **249**, 241 (2009).
5. V. O'Flaherty and E. Colleran, *Bioresour. Technol*., **68**, 101 (1999).
6. J.S. Hirasawa, A. Sarti, N.K.S. Del Aguila and M.B.A. Varesche, *Anaerobe*, **14**, 209 (2008).
7. K. Kosinska and T. Miskiewicz, *Bioresour. Technol*., **100**, 86 (2009).
8. M.K. Jain, M.C. Flickinger and S.W. Drew. Anaerobes Industrial Uses In Encyclopedia of Bioprocess Technology. New York: Wiley (1999).
9. H.H.P. Fang, Y. Liu and T. Chen, *J. Environ. Eng.*, **123**, 320 (1997).
10. G. Percheron, N. Bernet and R. Moletta, *Bioresour. Technol*., **61**, 21 (1997).
11. B.E. Rittmann and P.L. McCarty, Environmental Biotechnology-Principle and Applications, McGraw-Hill International Edition, Boston (2001).
12. M. Vossoughi, M. Shakeri and I. Alemzadeh, *Chem. Eng. Process*., **42**, 811 (2003).
13. V. O'Flaherty, T. Mahony, R. O'Kennedy and E. Colleran, *Process Biochem*., **33**, 555 (1998).
14. O. Mizuno, Y.Y. Li and T. Noike, *Water Sci. Technol*., **30**, 45 (1994).
15. M. Wu, F. Wilson and J.H. Tay, *Bioresour. Technol*., **71**, 151 (2000).
16. AWWA. Standard Methods for the Examination of Water and Wastewater (1992).
17. Ozturk I. Anaerobik biyoteknoloji ve atik aritimindaki uygulamalari. ITU Insaat Fak, Çevre Mühendisligi Bölümü: Su Vakfi Yayinlari (2000).
18. E. Genschow, W. Hegemann and C. Maschke, *Water Res*., **30**, 2072 (1996).
19. D.M. McCartney and J.A. Oleszkiewicz, *Water Environ. Fed.*, **65**, 655 (1993).
20. Y.-Y. Li, S. Lam and H.H.P. Fang, *Water Res*., **30**, 1555 (1996).
21. L.W. Hulshoffpol, P.N.L. Lens, J. Weijma and A.J.M. Stams, *Water Sci. Technol*., **44**, 67 (2001).
22. A. De Smul, L. Goethals and W. Verstraete, *Process Biochem*., **34**, 407 (1999).
23. J. Weijma, E.A.A. Bots, G. Tandlinger, A.J.M. Stams, L.W.H. Pol and G. Lettinga, *Water Res*., **36**, 1825 (2002).
24. M.H. Isa and G.K. Anderson, *Process Biochem*., **40**, 2079 (2005).
25. J. Shayegan, F. Ghavipanjeh and P. Mirjafari, *Process Biochem*., **40,** 2305 (2005).
26. E. Choi, J.M. Rim and E. Choi, *Water Sci. Technol*., **23**, 1259 (1991).
27. M.A. El Bayoumy, J.K. Bewtra, H.I. Ali and N. Biswas, *Water Air Soil Pollut*., **112**, 67 (1999).